Temporal and spatial changes in dissolved organic carbon concentration and fluorescence intensity of fulvic acid like materials in mountainous headwater catchments

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Abstract:

Dissolved organic carbon (DOC) such as humic substances are key to understanding the aquatic environment in catchments, because they, containing a large number of phenolic and carboxylic acid groups, adsorb many kinds of inorganic materials and also affect nutrition and carbon transport in catchments. To understand the detailed DOC dynamics, we conducted hydrological observations at mountainous headwater catchments dominated by different vegetation types (planted evergreen coniferous forest of 1.29 ha and natural deciduous broadleaf forest of 1.28 ha). The relationship between DOC concentrations and fluorescence intensity of fulvic acid-like materials (F-FAM) were positively correlated in both catchments but different between soil extracts, baseflow, and near surface flow represented by biomat flow. The ratios of change in F-FAM to that in DOC concentration (F-FAM/DOC) were higher in the baseflow (about 6 in both catchments) and lower in the soil extracts (about 4.5 in both catchments, respectively). However, the relationship in stormflow was distributed between the trends of baseflow and soil extracts. The higher F-FAM/DOC in baseflow may thus indicate that DOC (and FAM) in groundwater discharge mainly contributed to the stream flow, and the stormflow mainly reflect subsurface flow through soil during most rainstorms. In contrast, a high F-FAM/DOC ratio (>6) appeared in the stormflow of both catchments especially during large storms of short duration and high intensity following a dry antecedent period. The F-FAM/DOC in biomat flow developing distinctly in the coniferous catchment was high (about 6.5). Thus, rapid shallow subsurface flow through the biomat or near-surface of slopes might explain the unique transport dynamics of DOC and FAM in stormflows with the high F-FAM/DOC ratio. These results imply that the DOC and FAM relationship responds variably depending on both the distribution of soil organic matter and rainwater flow paths in steep slopes as well as on storm size and characteristics.

KEY WORDS: humic substance, biomat, preferential flow, stormflow, soil organic matter

1. Introduction

Variation of dissolved organic carbon (DOC) in stream water has been investigated in catchments of differing size and land use, but particularly in forested catchments, which are an important source of DOC (e.g., Beynen et al., 2000; Hagedorn et al., 2000; Perakis and Hedin, 2002; Piatek et al., 2009) and thus of nutrition and carbon materials. These studies have revealed that most DOC was flushed into streams by stormflow. The relationship between patterns of stream flow discharge and DOC concentration often reflects the process by which DOC enters a stream. Typically, the peak DOC concentration coincides with, or occurs slightly before, the peak stormflow discharge (e.g., Inamdar and Mitchell, 2006) or the peak snowmelt discharge (e.g., Boyer et al., 1997; Sakamoto et al., 1999; Creed et al., 2008). In addition, DOC concentrations in stormflow were higher during rainstorms in the dry season than during rainstorms in the rainy season (Inamdar et al., 2008).

DOC transport into streams depends on rainfall magnitude, the distribution of DOC in soil, the soil water content (Cooper et al., 2007), and the water flow path in catchments (e.g., Mulholland and Hill, 1997; Hagedorn et al, 2000; Katsuyama and Ohte, 2002; McGlynn and McDonnel 2003; Perakis and Hedin, 2007). Thus, the physical and chemical characteristics of DOC vary among catchments (e.g., Hope et al., 1997a, 1997b; Nagao et al., 2003; Cumberland and Baker, 2007, Fellman et al., 2009), implying that the dynamics of DOC in hydrological systems from slopes to streams needs to be understood on the basis of both environmental conditions in a catchment (topography, geology, vegetation, and climate) and the variation of DOC in the source area.

Fulvic acid (FA), which are soluble in water under all pH conditions (Aiken, 1985), accounts for 60% to 80% of DOC in stream water (Thurman, 1985; Malcolm, 1990). Thus, compared to the other components of DOC (e.g., humic acids which are insoluble in aqueous solution at pH lower than 2 (Aiken, 1985), proteins, carbohydrates, lipids, oxalate, formic acid, and other such materials), FA or fulvic acid-like materials (FAM), play a relatively important role in adsorbing and transporting ions, heavy metals, and radionuclides by complexation (e.g., Kim, 1985; Weber, 1988) in natural freshwater environments, and are also important for pollutant remediation, nutrient supply, and consequently in controlling the chemical properties of aquatic environments.

Headwater catchments, having only a first order stream, are the basic topographic unit in catchment hydrology, and the catchments dominated by different vegetation types may differ with regard to stream flow generation, owing to differences in the amount of throughfall and evapo-transpiration, water storage mechanisms in soil, and flow pathways on slopes (e.g., Swank and Crossley, 1988). In particular, headwater catchments are one of the primary sources of DOC, and the DOC dynamics can be strongly controlled by differences in slope hydrology in headwater catchments, as well as the dominant vegetation in these catchments. For example, based on the discussion of hydrological processes in each micro-topographic unit of headwater catchments, Katsuyama and Ohte (2002) and McGlynn and McDonnel (2003) reported the DOC export dynamics in small headwater catchments (a few ha in area) and indicated the hydrological importance of riparian zones affecting to the DOC export paths during rain storms. However, studies in headwater catchments, focusing specifically on the relationship between DOC and FAM transport, have been very few, and little is known about the effect of slope hydrology on the detailed DOC dynamics in headwater catchments. Therefore, discussion related to the relationship between DOC and FAM transport under high temporal resolution, which is appropriate for investigating the process of DOC and FAM transport during rainstorms in relation to rainfall intensity, storm discharge, and slope hydrology, is indispensable to understand the detailed DOC dynamics in headwater catchments. Additionally, fundamental information on DOC and FAM transport in relation to vegetation differences in headwater catchments may provide important knowledge to explore the variation of DOC component, bioavailability, and eventually their transport process in large catchments (e.g., Mulholland and Hill, 1997; Hagedorn et al., 2000; van Verseveld et al., 2009), which are assemblages of headwater catchments.

Then, to understand the influence of vegetation types and consequent slope hydrology on detailed DOC dynamics in headwater catchments, we collected samples of stormflow (i.e., stream flow during rainstorms) at 1-h intervals during six rainstorms in two adjacent headwater catchments with similar topography, geology, and climate, but different vegetation types (evergreen coniferous trees and natural deciduous broadleaf trees). Additionally, for specific understanding of DOC and FAM transport during rainstorms, we collected soil and baseflow samples in both catchments at days without precipitation and biomat flow samples from the slope of a coniferous forest at irregular intervals during summer rainstorms. We subsequently measured the DOC concentration and fluorescence intensity of FAM in the samples of soil extracts, baseflow, stormflow, and biomat flow and then discussed the DOC dynamics in the mountainous headwater catchments with steep slopes.

2. Site description

2.1. Geology, topography, and climate

Our study was conducted in the Nariki catchment. The topography of the Nariki catchment and the location of two headwater catchments that we studied are shown in Figure 1. The Nariki catchment (35˚50′N, 139˚10′E; Figure 1a) is about 40 km west of central Tokyo, at the southeastern edge of the Kanto mountains, which have maximum heights of about 2500 m. Slope gradients in the catchment range between 35° and 45°, and Mt. Kuro-yama, at 842 m, is the highest point. The catchment is underlain by sandstone and mudstone bedrock of Jurassic age that also contains some chert. The rock units dip 60° to 90° northeast and strike NW-SE (Inosato et al., 1980; Tokyo Prefectural Public Work Institute, 2002).

Data collected at the Automated Meteorological Data Acquisition System (AMeDAS) station of the Japan Meteorological Agency at Ohme City (35°47′N, 139°18′E; 10 km southeast of the Nariki catchment and 100 m in elevation) show that the average annual precipitation from 1976 to 2009 was 1487 mm, and the minimum (late January), maximum (mid-August), and average annual air temperatures were –6.7 ˚C, 36.9 ˚C, and 14.2 ˚C, respectively. Rainstorms usually occur in the rainy season from mid-June to late July, and in the typhoon season from mid-August to mid-October. About 80% of the annual precipitation is supplied during these periods. Dry conditions prevail in winter, from early December to early March, although snow usually accumulates in the Nariki catchment to a maximum depth of 10 to 20 cm in February.

2.2. Experimental catchments

A headwater catchment on the north side of the Nariki River was densely planted with evergreen coniferous trees in 1961 (Coniferous catchment in Figures 1a and 1b). It is 1.29 ha (0.0129 km^2) in area, 100 m in relief, and includes only a first-order stream. This unmanaged forest is composed of Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*), and in 2007 there were 2000 to 2500 trees ha^{-1}, all with trunk diameters of less than 0.2 m. The canopy of the forest is mostly closed, and little understory vegetation is present owing to the weak penetration of sunlight to the forest floor. A gravel rich mineral soil (B-horizon) is directly exposed on parts of the forest floor.

A second headwater catchment on the south side of the Nariki River is covered by a natural deciduous broadleaf forest (Deciduous catchment in Figures 1a and 1c). The catchment area is 1.28 ha (0.0128 km^2), 100 m in relief, and has only a first-order stream. The dominant tree species in this catchment are oak (*Quercus serrata* and *Q. mongolica*), beech (*Fagus japonica*), chestnut (*Castanea crenatus*), and Japanese maple (*Acer palmatum*). Understory vegetation is relatively dense, and there is a thick litter layer (about 5 cm in thickness) on the forest floor (Figure 2b).

2.3. Physical properties of soil

The boundary between soil and bedrock, obtained by N_{10} values (the number of blows for 10 cm penetration into soil by cone penetration test using a weight of 5 kg) showed that the soil depth ($N_{10} \leq 50$) was less than 3 m in both catchments and the soil profiles to cross and longitudinal section of the catchments have similar shapes in both catchments. Both cross section topographies of the catchments are V-shaped, and consequently the riparian zone (the flat bottomland along the streams), affecting stream flow generation, is very small and narrow (Figures 1b and 1c).

Mid-slope soil profiles in each catchment are shown in Figure 2. According to the classification by the Food and Agriculture Organization of the United Nations, the soils in both catchments were classified as Cambisols. The strongly organic soil horizons, the A_0 to AB horizons, were up to 0.25 m thick in both catchments, and a gravel rich mineral soil (B horizon) was below 0.15 to 0.25 m depth. The soil parent material presumably derived from up-slope via soil creep or rock slides, because much discrete angular gravel was observed in the soil profiles.

We collected undisturbed 100 mL soil cores (about 5 cm long and 5 cm in diameter) at soil surface and at 30 cm intervals from 20 to 140 cm depth at the up-, mid-, and down-slopes in the catchments. Soil pH within 140 cm depth ranged mostly between 4 and 5.

The average saturation hydraulic conductivity (Ks) of the soil in both catchments ranged mostly between 10^{-2} and 10^{-3} cm s^{-1}: it decreased to 10^{-4} cm s^{-1} at 30 cm depth of the up- and mid-slopes in the coniferous catchment, indicating relatively low permeability, whereas it was constant (around 10^{-2} cm s^{-1}) in the deciduous catchment regardless of soil depth.

Average soil porosity of the coniferous catchment (in this case, it was obtained from the weight difference in the soil cores between water saturated and dried conditions heated for 24 h at 110 °C) ranged between 78% at the soil surface (including a biomat described in the section 2.4) and 45% at 70 cm depth, whereas that of the deciduous catchment was between 73% around the soil surface (also including the biomat) and

53% at 70 cm depth.

Average soil hardness in the coniferous catchment (measured at five random points on the soil profiles at 5 cm intervals and up to 50 cm depth) ranged from 10 kPa at the soil surface (corresponding to the biomat) to 250 kPa at 50 cm depth with showing the maximum hardness of 600, 300, and 400 kPa at 30 cm depth of the up-, mid-, and down-slopes, respectively, whereas that in the deciduous catchment increased uniformly from 40 kPa at the soil surface to a maximum of 200 kPa at 50 cm depth.

The gravitational water drainage capacity of the soil was 18% on average in the coniferous catchment except between 0 and 5 cm depth, where it was 28% on average (including the biomat). In the deciduous catchment, it was constant at 25% on average throughout the soil profile.

2.4. Biomat features

A unique layer, the so-called biomat (BM: Ks > 10^{-2} cm s^{-1}; porosity above 70%), consisting of a dense network of fine roots within the loose litter and root-permeated zone (Sidle et al., 2007), was common at the slope surface in the coniferous catchment, where its thickness varied from a few centimeters to 20 cm (Figure 3a).

In the coniferous catchment, the average root density in the biomat (weight of root per unit weight of biomat) was 6.37 g kg^{-1} and 9.15 g kg^{-1} for each 5 sample in the two biomat plots shown in Figure 1b, which had the biomat of about 3 and 10 cm thick, respectively. In contrast, the root density in the soil, just below the biomat (upper A horizon: 5 to 10 cm depth and 10 to 15 cm depth for the plots with the biomat of 3 and 10 cm thick, respectively), was 0.19 g kg^{-1} and 0.30 g kg^{-1}, respectively; about 3% of the corresponding values in the biomat.

Although the biomat was indistinguishable in the deciduous catchment, being no more than a few centimeters thick, the average root density was 6.94 g kg^{-1} in the biomat where it was 3 cm thick, similar to that of the biomat in the coniferous catchment. The root density in the soil (upper A horizon), just below the biomat of 3 cm thick, was 1.78 g kg^{-1}, about 26% of the density in the biomat; indicating that, compared to the coniferous catchment, relatively indistinct boundary between the biomat and the upper A horizon was provided in soil profiles of the deciduous catchment.

Hirano et al. (2008) first reported that water flow occurred in biomats during rainstorms, accounting for 5% to 40% of the rainfall, reaching 30 cm s^{-1} in maximum flow velocity, and occurring dominantly following dry antecedent periods; they called such flow "biomat flow". It is a strong preferential flow path for rapid rainwater transport on slopes, especially in the unmanaged coniferous (Hinoki cypress) forests of Japan and usually in the deciduous forests due to the relatively constant root permeated zone around the shallow portion of soil, showing the near-surface flow path (e.g., Tamura et al., 2002; Sidle et al., 2007).

3. Instrumentation and data collection

3.1. Rainfall

The locations of the observation devices are shown in Figure 1. The rain gauge (0.2 mm $count^{-1}$: Figure 1a), which recorded the precipitation at 5-min intervals, was installed in an open space near the catchments (710 m elevation) where rainfall was not intercepted by the tree canopies because of no canopies beyond 45 degree in elevation.

Average annual rainfall interception by the tree canopies in the coniferous and deciduous catchments (from April 2005 to March 2006) was 18.7% and 15.7% of the total rainfall measured by the rain gauge, respectively.

Observed six rainstorm events are listed in Table 1. The rainstorms were classified as small (Storm 1, Storm 2), medium (Storm 3, Storm 4), or large (Storm 5, Storm 6) according to whether the total precipitation during the storm was around 20, 40, or more than 70 mm. The AMeDAS data from Ohme City show that rainfall amounts of more than 1 mm day^{-1} occurred on 109.1 days yr^{-1} on average from 1976 to 2009, and the average frequencies of rainy days from 1976 to 2009 with the total precipitation amounts of Storm 1 to Storm 6 were 28.5, 28.5, 8.2, 28.5, 1.2, and 2.9 days yr^{-1}, respectively. Antecedent precipitation for 7 and 14 days prior to the corresponding rainstorms (API-7 and API-14) showed that, within the same rainstorm scale, the antecedent periods were relatively dry before Storm 1, Storm 4, and Storm 5 and relatively wet before Storm 2, Storm 3, and Storm 6.

3.2. Stream flow (baseflow and stormflow)

Stream flow in the catchments was measured by parshall flumes (6 inch [15 cm] size) installed in the streams at the mouths of each catchment (Figures 1b and 1c). Water levels in the flumes were recorded at 5-min intervals by automatic sensors (Trutrack, WT-HR64K, USA). The relationship between the water levels and the stream flow discharge manually measured at the flumes, the H-Q relation, was used to calculate the stream flow (Ls^{-1}) throughout the observation period. The baseflow before the rainstorms in the deciduous catchment ranged between 1 and 1.94 times that in the coniferous catchment (Table 1).

Stormflow samples from the catchments were automatically collected at the upstream side of the flumes in polyethylene bottles by automatic water samplers (American SIGMA; Model 900, USA) at 1-h intervals during the six rainstorms. Glass bottles were also used for intermittent manual sampling of the stormflow and baseflow, and the fluorescence intensity of those samples was compared with that of the samples collected in the polyethylene bottles; the difference in measured normalized fluorescence intensity of FAM (F_m-FAM described in the section 3.5) were below 0.1 QSU, implying that no influence to the fluorescence intensity was brought by the difference in collection materials.

3.3. Biomat flow

The biomat and observation devices for measuring biomat flow in a coniferous forest are shown in Figures 3a and 3b. It was difficult to install the observation devices in the coniferous catchment on account of steep slopes and the exposure of basement rocks along the stream. Thus, we chose two observation sites outside but close to the coniferous catchment (Figures 1a and 1b), that located at the foot of a topographically planar slope about 30 to 40 m east of the parshall flume in the coniferous catchment, 2 m above and about 3 m distance from the Nariki River, where vegetation (Hinoki cypress forest) and soil properties were same as those in the coniferous catchment.

The thickness of the biomat at the observation sites was from 10 to 15 cm (Figure 3a). Biomat flow was collected at irregular time intervals during summer rainstorms in 2009 by fixing polyvinyl chloride (PVC) troughs of 70 and 120 cm in length along the boundary between the biomat and upper A horizon (Figure 3b). To avoid overland flow contamination, the overland flow was separately collected by fixing other troughs on the slope surfaces. No overland flow, however, was generated not only around the observation sites but also on the whole slopes of the coniferous and deciduous catchments during the observation period. The collected biomat flow was directed into tipping buckets through PVC tubes and measured at 5-min intervals. After the flow measurement, the water was drained into glass bottles through the PVC tubes and used for the measurements of DOC concentration, excitation-emission matrix fluorescence spectrum (EEM spectrum), and ultraviolet-visible spectrum (UV spectrum).

3.4. DOC and FAM

The collected soil samples were air-dried (see the section 2.3 for the collection method) and subsequently 3 g of the samples was shaken for 24 h in 60 mL of ultrapure water obtained from a water purification system (RFU585DA, Advantech, Japan; pH 5.6, 18.2 MΩ cm, and DOC < 0.01 μg L^{-1}). Then, the soil extracts and baseflow was filtered for the measurements of pH, DOC, EEM spectrum, and UV spectrum. The absolute values of the DOC concentration and EEM spectrum in soil extracts are variable on account of the measurement method based on the proportion of air-dried soil weight relevant to ultrapure water volume. Thus, the values of DOC concentration and EEM spectrum in soil extracts are impossible to compare directly with those in stream flow and biomat flow, whereas it is possible to compare the correlations in soil extracts with those in stream flow and biomat flow, because the measurement method does not affect to the correlations between the DOC concentration and EEM spectrum of soil extracts.

In contrast, in our study, water samples collected in polyethylene bottles were transferred to glass bottles as soon as possible and all collected water samples were stored at 4 °C within one day of collection. The samples were subsequently filtered through 0.45-µm mixed cellulose aster filter (DISMIC-25AS, Advantech, Japan) within 5 days after collection, and the DOC concentrations and EEM and UV spectra in the filtrate were measured. The DOC concentration of the water samples was measured with an organic carbon analyzer (TOC-V, Shimadzu, Japan). The EEM spectra of undiluted water samples were measured with an EEM spectrometer (xenon excitation source; FP-6600, JASCO, Japan), under excitation wavelengths of 220–550 nm, emission wavelengths of 250–600 nm, and a scanning speed of 2000 nm min^{-1}. Transparent quartz glass cells (inside width is 1 cm) were arranged for the water samples into the EEM spectrometer. The peak fluorescence intensity of the water samples was similarly normalized in our study relative to the fluorescence intensity of FAM determined on the basis of the fluorescence intensity of 10 µg L^{-1} quinine sulfate solution (10 QSU) at Ex 345 nm, Em 440 nm, of which the solvent (sulfuric acid, 0.1 mol L^{-1}; Wako Pure Chemical Industries, Japan) exhibited no fluorescence spectrum.

Malcolm (1985) showed that the peaks in fluorescence intensity of river humic substances occurred at excitation wavelengths of 320–350 nm and emission wavelengths of 420–440 nm (Ex 320–350 nm, Em 420–440 nm). In addition, fluorescence peaks within the above ranges have been identified as FAM peaks (Coble et al., 1993; Suzuki et al., 1998; Mostofa et al., 2005). In our measurements, a single peak in fluorescence intensity appeared at Ex 330–345 nm, Em 428–446 nm in each stream flow sample from the coniferous catchment, and at Ex 300–345 nm, Em 432–446 nm in each sample from the deciduous catchment. These peaks correspond to "Peak C" indicated by Coble et al. (1990), Coble (1996), and Fellmann et al. (2010), and could reflect terrestrially organic matter (Cory et al., 2010) derived from vascular plants or soil organic matter which is high-molecular-weight fraction and highest in wetlands and forested environment (Cobol et al., 1998). Some water samples in the coniferous catchment and soil extracts in both catchments exhibited another peak at around Ex 270 nm, Em 320 nm corresponding to "Peaks B or T" indicated by Fellmann et al. (2010), possibly corresponding the amino acid-like peaks in tyrosine or tryptophan, respectively (e.g., Coble et al., 1993, Parlanti et al., 2000). No peaks in humic like- and unknown- materials appeared in stream flow samples at all.

3.5. Correction of fluorescence intensity

The identical instrument was used for our measurement, and the fluorescence intensity of the quinine sulfate solution was verified every 140 min (for every batch of seven water samples). To determine the instrumental errors which may have been caused by fluctuations in illumination, the fluorescence intensity of the water samples was subsequently normalized on the basis of the average QSU values of the 10 μg L^{-1} quinine sulfate solution obtained before and after the measurement of seven water samples (the maximum difference was 0.64 QSU). In our study, the correlation line of the measured normalized fluorescence intensity of FAM (F_m-FAM: without the inner filter correction) relative to DOC concentration became convex at DOC > 22 mg L^{-1} and F_m-FAM > 120 QSU, indicating that attenuation of the FAM spectra of the water samples, due to high FAM concentration, probably began at values greater than 120 QSU. Thus, the samples which exceeded 120 QSU were omitted from our analysis.

In contrast, Yang and Zhang (1995) indicated that the inner filtering effect in water was minimized under the DOC concentration below 15 mg L^{-1}. In addition, Hudson et al. (2007) also indicated that the inner filtering was found to be negated in freshwater samples. In our measurement, the F_m-FAM was simultaneously corrected for the inner filtering effect according to the following equation (Lakowicz, 1999):

$$F_c = F_m \cdot 10^{(A_{ex} + A_{em})/2}$$

where F_c is the corrected normalized fluorescence intensity of FAM (F_c-FAM), F_m is the measured (uncorrected) normalized fluorescence intensity of FAM (F_m-FAM), A_{ex} is the absorbance at excitation wavelength, and A_{em} is the absorbance at emission wavelength.

The measurement error of the fluorescence intensity of 10 μg L^{-1} quinine sulfate solution in our study ranged between 0.16 QSU and 0.64 QSU for the observed Storms. In contrast, the correction coefficients ($10^{(A_{ex} + A_{em})/2}$) around EX 340nm, Em 440nm of the baseflow and stormflow were calculated as less than 1.03 below 20 QSU, producing a 0.6 QSU in maximum rise of F_m-FAM at 20 QSU. This thing implies that, in our study, the rises of F_m-FAM resulted from the inner filter correction are within the measurement error of the fluorescence intensity of 10 μg L^{-1} quinine sulfate solution. Consequently, for the baseflow and stormflow at F_m-FAM < 20 QSU, the inner filter correction is found not to cause the significant inconsistency between F_c-FAM and F_m-FAM and to be negligible. Accordingly, in our study, the inner filter correction was conducted both for water samples of F_m-FAM exceeding 20 QSU and for all soil extracts of which the high absorbance at around 420 nm produced the correction coefficients exceeding 1.06

even at F_m-FAM < 20 QSU; we corrected both the F_m-FAM of biomat flow (20 QSU < F_m-FAM < 120 QSU) and all soil extracts (F_m-FAM < 120 QSU), and did not correct the F_m-FAM of baseflow and stormflow of which the most F_m-FAM was below 20 QSU.

Additionally, we measured the absorbance for the wavelengths of 200 nm to 600 nm with an ultraviolet-visible spectrophotometer (V570, JASCO, Japan) at 1 nm interval. Then, to minimize the measurement error of the EEM spectra, water samples of which the absorbance at 254 nm (Abs-254) was below 0.3 (Cory et al., 2010) were used in our analysis and discussion. The range (Abs-254 < 0.3) is equivalent to the F_m-FAM below 50 QSU in our study.

4. Results

4.1. DOC vs. FAM relationships in soil extract, baseflow, and biomat flow

The relationships between DOC concentrations and fluorescence intensity of FAM (F-FAM: including both the F_m-FAM of baseflow and stormflow and F_c-FAM of soil extracts and biomat flow) in biomat flow of the coniferous catchment, as well as those in the soil extracts and baseflow in the two catchments, are shown in Figure 4.

Soil extracts at F-FAM < 20 QSU in Figure 4 were mostly obtained from the soil collected below 50 cm depth (relatively deep soil layer). The relationship between the DOC concentration and F-FAM (DOC vs. FAM relationships) with respect to soil extracts were positively correlated and the trend (correlation) lines were expressed by dashed lines as $y=4.91x-22.68$ ($n=27$, $r=0.84$, $p<0.0001$) and $y=4.14x-20.02$ ($n=16$, $r=0.89$, $p<0.0001$) in the coniferous and deciduous catchments, respectively. Significant difference in the DOC vs. FAM relationships with respect to soil extracts between the coniferous and deciduous catchments appeared in both the DOC concentration ($p<0.0001$) and F-FAM ($p<0.0001$).

The DOC concentration and F-FAM in baseflow ranged mostly from 0.5 to 3 mg L^{-1} and 2 to 14 QSU in both catchments, respectively. The DOC vs. FAM relationships with respect to baseflow were positively correlated and the trend lines were expressed by solid lines as $y=6.09x-0.90$ ($n=48$, $r=0.90$, $p<0.0001$) and $y=5.60x-2.37$ ($n=50$, $r=0.84$, $p<0.0001$) in the coniferous and deciduous catchments, respectively. Significant difference in the DOC vs. FAM relationships with respect to baseflow between the coniferous and deciduous catchments appeared not in the DOC concentration ($p=0.8026$) but in the F-FAM ($p=0.0197$).

In addition, the DOC vs. FAM relationships with respect to biomat flow was plotted at the upper end of the baseflow trend lines and the biomat flow trend line was expressed by a solid line as $y=6.50x-4.88$ ($n=21$, $r=0.73$, $p<0.0001$). Thus, the slope of biomat flow trend lines was very high, even higher than that in the baseflow (6.09 and 5.60 in the coniferous and deciduous catchments, respectively) but were clearly different from those of soil extracts (4.91 and 4.14 in the coniferous and deciduous catchments, respectively).

4.2. Temporal changes in DOC and FAM in stormflow

Temporal changes in specific stream flow (stormflow), DOC concentration, and F-FAM during the representative rainstorms (Storm 1, Storm 3, and Storm 5) are shown in Figure 5 (refer to Figure 6 for Storm 2, Storm 4, and Storm 6).

In Storm 1, low-intensity rain less than 1 mm 5 min^{-1} fell following relatively dry antecedent periods (Table 1). On the other hand, Storm 2 occurred following relatively wet antecedent periods because it followed five successive rainstorms from September 11 to 15, 2006 that had a total precipitation of 124 mm (Table 1). Prominent stormflow peaks coinciding well the timing of the rainfall peaks were not observed during Storm 1 and Storm 2. In Storm 1 (Figure 5a), the changes in DOC concentrations of both catchments were similar to background of baseflow (0.5 to 3 mg L^{-1}) despite of relatively large increase in F-FAM which was slightly higher in the deciduous catchment (12 QSU in maximum F-FAM) than in the coniferous catchment (9 QSU in maximum F-FAM). In contrast, in Storm 2 (refer to Figures 6a and 6d), the DOC concentration consistently exceeded 3 mg L^{-1}, higher than that in Storm 1, and the F-FAM ranged between 2 QSU to 5 QSU in both catchments, similar or lower than that in Storm 1. Thus, even though the two storm events were similar in the rainstorm scale (Table 1), DOC concentrations were higher in Storm 2 following the relatively wet antecedent periods than in Storm 1 following the relatively dry antecedent periods.

In Storm 3, following relatively wet antecedent periods (Table 1), the rainfall continued for about 24 h, and its intensity was 1 to 2 mm 5 min^{-1}. In contrast, Storm 4 following relatively dry antecedent periods lasted about 40 h (Table 1), and its intensity was less than 1 mm 5 min^{-1}. The changes in DOC concentrations and F-FAM in Storm 3 tended to coincide with the changes in stormflow (Figure 5b). Flash rises of DOC concentration and F-FAM at 7:30 LT on September 27 in Storm 3 coincided with the flash peaks in stream flow (about 1 L s^{-1} ha^{-1}) at the same time in both catchment. The changes in DOC and F-FAM in Storm 4 were similar to those in Storm 3 except the two cases indicated by arrows in the coniferous catchment (refer to Figures 6b).

During Storm 5, high-intensity rain exceeding 2 mm 5 min^{-1}, fell for 9 h following relatively dry antecedent periods (Table 1). The hydrograph recession in Storm 5 (Figure 5c) was rapid and high stormflow discharge did not continue very long after the rainfall ended (for 15 h and 4 h at most after the flow peaks until the stormflow receded below 1 L s^{-1} ha^{-1} in the coniferous and deciduous catchments, respectively). Two remarkable flash rises of F-FAM with high rainfall intensity and flash rises of stormflow were observed in both catchments at the early stage of the storm (at 2:55 LT and 6:45 LT on August 9). In contrast, Storm 6 had a long-duration rainfall (about 48 h) following relatively wet antecedent periods with a moderate intensity of 1 to 2 mm 5 min^{-1} (Table 1), high stream flow discharge for a long time in both catchment (more than 5 days after the stormflow peaks until the stormflow receded below 1 L s^{-1} ha^{-1}), and rare flash flow peaks. Except the cases in the flash rises of F-FAM in Storm 5 (> 13 QSU), the F-FAM in Storm 6 (1 to 12 QSU) was similar to that in Storm 5 (refer to Figures 6c and 6f). However, the DOC concentrations in Storm 6 was higher (2 to 8 mg L^{-1}) than those in Storm 5 (0.5 to 3 mg L^{-1}).

4.3. DOC vs. FAM relationships with respect to stormflow

The DOC vs. FAM relationships with respect to stormflow during the six rainstorms are shown in Figure 6, in which the solid and dashed lines show the trend lines of the baseflow and soil extracts shown in Figure 4, respectively.

The DOC vs. FAM relationships in Storm 1 (Figures 6a and 6d), under the small-scale rainstorm following relatively dry antecedent periods, were close to the baseflow trend lines in both catchments. In Storm 2, under the small-scale rainstorm following relatively wet antecedent periods, the data in both catchments was plotted near the bottom of the soil extract trend lines.

In Storm 3 and Storm 4 (Figures 6b and 6e), the DOC vs. FAM relationships ranged between the baseflow and soil extract trend lines in both catchments. However, in comparison with the other data in Storm 4, following relatively dry antecedent periods, some relationships in the coniferous catchment in Storm 4 (indicated by arrows in Figure 6b) were characterized by the high F-FAM with respect to DOC concentration, coincided with the flash peaks in the F-FAM and stormflow.

In Storm 5 (Figures 6c and 6f), following relatively dry antecedent periods, the DOC vs. FAM relationships were close to the baseflow trend lines, and the F-FAM rose considerably above the trend line at 13 QSU < F-FAM < 18 QSU (circled in Figure 6c and 6f). Despite the high rainfall amount and the generation of high stormflow by this rainstorm, DOC and FAM in the stormflow seemed to result entirely from baseflow. In contrast, in Storm 6, the DOC vs. FAM relationships were close to the soil extract trend line in the coniferous catchment and between the baseflow and soil extract trend lines in the deciduous catchment, similar to the relationships in Storm 3 and Storm 4 except the high F-FAM exceeded 10 QSU.

5. Discussion

The distinct differences in the DOC vs. FAM relationships among soil extracts, baseflow, and biomat flow, as well as their various correlations during the rainstorms, exhibit that the complicated processes in DOC transport occurred even if the headwater catchments was relatively small as including only the first order streams. Thus, as given below, to understand the various relationships between DOC and FAM transport, we examine the DOC dynamics and discuss the different views between our findings and other studies, regarding DOC and FAM export resulted from rainfall input (Park et al., 2007) and antecedent hydrological conditions (Inamder et al., 2008). In addition, we consider how the preferential flow affects DOC transport in the headwater catchments with steep slopes, and consequently propose the hydrological regime affecting the DOC vs. FAM relationships in mountainous headwater catchments.

5.1. Dynamics of DOC and FAM transport

The F-FAM/DOC in the soil extracts of the coniferous catchment, shown in Figure 4, tended to be higher (F-FAM/DOC=4.91) than that in the deciduous catchment (F-FAM/DOC=4.14), and the significant differences were shown both in the DOC concentration ($p<0.0001$) and F-FAM ($p<0.0001$). Because of their adjacent locations, the two catchments are similar with respect to catchment area, elevation, slope gradient (but not direction), and geology. Thus, the difference in the F-FAM/DOC in the soil extracts may have been due to the degradation degree of organic materials into DOC, faster or more in the deciduous catchment than in the coniferous catchment (e.g., Olson, 1963; Kawahara, 1985).

Additionally, the difference in the F-FAM/DOC between the baseflow (6.09 and 5.60 in the coniferous and deciduous catchments, respectively) and soil extracts (4.91 and 4.14, respectively) suggest that FAM was the more dominant DOC material in the baseflow than in the soil extracts (Figure 4). FAM is the refractory soil organic matter and consequently can be remained uniformly as decomposed residues in the deep part of soil (Boyer and Groffman, 1996) and consequently in the baseflow. The soil extracts had the high absorbance at 420 nm, and additionally in our other analysis (unpublished), much of the organic nitrogen was contained in the soil extracts while it was little in the baseflow. Thus, the increase in the F-FAM/DOC in the baseflow is probably due to the stabilization or decomposition of humic acid like materials (HAM) within the soil layer, though HAM was not detected in the EEM spectrum of soil extracts.

The shift in the DOC vs. FAM relationships with respect to stormflow toward the lower end of the soil extract trend lines (Figure 6) means that, compared to the DOC concentration in baseflow (0.5 to 3 mg L^{-1}, Figure 4), the DOC concentration in stormflow was predominantly increased in Storm 2, Storm 3, Storm 4, and Storm 6 (2 mg L^{-1} to 7 mg L^{-1}), whereas the changes in F-FAM, except that in Storm 5, ranged from 1 QSU to 13 QSU (Figure 6), which was within the similar range of baseflow (2 QSU to 14 QSU, Figure 4). That is, only the DOC concentration increased in the stormflow under the relatively constant F-FAM. These facts can be due to the DOC and FAM transport during the rainstorms from the deep part of soil below 50 cm depth which shows relatively higher DOC concentration than that of baseflow. This may depend on HAM discharge containing in the soil which showed the absorbance at 420 nm, and seems to be contrary to the finding of Park et al. (2007) that the FA concentration was higher in stormflow than in baseflow in forested headwater catchments. In Park et al. (2007), the detailed DOC dynamics has not been explained on the basis of hydrological processes in the micro-topographic units of their headwater catchment. Thus, the simple comparison of our findings with those of Park et al. (2007) is impossible. We guess that the reason of the differing view may result from the difference in hydrological systems between their and our headwater catchments, depending possibly on the topographic difference represented by the distribution of riparian zone affecting the DOC export paths (very narrow in our catchments), slope gradient (very steep in our catchments as between 35° and 45°), or the size of the headwater catchment (a few ha in our catchments).

The high DOC concentration appeared in Storm 2 following relatively wet antecedent periods. These findings are contrary to the observation by Inamdar et al. (2008) that DOC concentrations in river flow were higher in stormflows following dry antecedent periods than wet antecedent periods. They indicated that the size of the available pool of DOC relevant to the volume of rainfall input may have been an important factor to control the DOC concentration in stormflows, as represented by the mobility of DOC fraction (i.e., the release of a greater proportion of carbon rich hydrophobic dissolved organic matters). Although the reason of differing views between the observations by Inamdar et al. (2008) and our findings is unclear yet, it may depend on the variable DOC dynamics in headwater catchments, resulted possibly from the rainfall condition (small scale in Storm 2 accompanied with very small rise of stormflow even following relatively wet antecedent periods) and the difference in headwater topography controlling the DOC source and path, because, in the headwater catchments in Inamdar et al. (2008), the relief is smaller (about 50 m) and the slope is more gentle (15 degree) than those in our catchments (about 100 m and 35 to 45 degree, respectively).

5.2. Effect of biomat and near-surface soil on DOC and FAM transport

The F-FAM/DOC in biomat flow (Figure 4) also indicates that FAM was the more dominant DOC material in biomat flow than in the soil extracts. When we considered the DOC vs. FAM relationship with respect to soil extracts, obtained only from the soil surfaces containing the biomat in the coniferous catchment, the trend line is expressed as $y=5.34x$ (n=5, r=0.81, $p<0.0149$). This fact shows that the F-FAM/DOC in the soil extracts when only soil surfaces containing the biomat are taken into account (F-FAM/DOC=5.34) is closer to the F-FAM/DOC in the biomat flow (F-FAM/DOC=6.50), as opposed to all soil extracts (F-FAM/DOC=4.91 and 4.14 in the coniferous and deciduous catchments, respectively), though the mechanism flushing DOC and FAM out of the biomat or near-surface soils requires further consideration.

The flash peaks in stormflow and F-FAM selectively reflected periods of high rainfall intensity during Storm 5 which was high-intensity rain following relatively dry antecedent periods (Figure 5c). The ratio of direct runoff to total stormflow at the time of the second flash flow on the hydrograph (at 6:45 LT on August 9 in Figure 5c) was 94% and 32.8% in the coniferous and deciduous catchments, respectively (based on the hydrograph separation by use of the electric conductivity of stream flow by Hirano et al., 2008). This may indicate that the preferential flow through the biomat layer or near-surface soil, especially in the coniferous catchment, occurred under high rainfall intensity, even though litter accumulation was small, understory vegetation was sparse, and overland flow was not generated during the observation period. Therefore, much of FAM at this time would have been released and transported into the streams by hydrological processes at or near the soil surface in both catchments. In addition, the DOC vs. FAM relationships in Storm 5 was distributed above the baseflow lines (Figures 6c and 6f) and between the baseflow and biomat flow trends (13 QSU $<$

F-FAM < 18 QSU). Consequently, the DOC vs. FAM relationships at 13 QSU < F-FAM < 18 QSU in Strom 5 could be strongly influenced by the direct runoff as biomat flow or other near-surface preferential flow, in addition to groundwater discharge. This was similar to the two cases in the coniferous catchment in Storm 4 (arrow in Figure 4b), following relatively dry antecedent periods, which were characterized by the high F-FAM with respect to the DOC concentration.

As described in the section 2.4, the root density in the upper A horizon in the coniferous and deciduous catchments was respectively 3% and 26% of the root density in the biomat. These differences imply that the boundary between the biomat and upper A horizon was more distinct in the coniferous than in the deciduous catchment, as well as the distinct differences in the physical properties of soil between the soil surface and upper A horizon in both catchments (i.e., saturation hydraulic conductivity, soil porosity, soil hardness, and gravitational water drainage capacity described in the section 2.3). In addition, the differences in root density suggest that subsurface lateral flow in the shallow soil of the deciduous catchment, comprising not only the thin biomat but also the upper A horizon with the root density of 1.78 g kg^{-1}, corresponding to about 26% of the density in the biomat, might play an important role in the rapid transport of rainwater along slope surfaces, (e.g., Brown et al., 1999; Tamura et al., 2002; Kim et al., 2005). This preferential flow may be provided especially in steep slopes that seem to be more reason for promoting not vertical rainwater infiltration but lateral shallow subsurface flow along the root systems. Thus, as well as the hydrological importance of the riparian zone affecting the DOC export paths (Katsuyama and Ohte, 2002; McGlynn and McDonnel, 2003), biomat flow, particularly in the coniferous catchment, and near-surface flow in the deciduous catchment, may account for most transport of FAM into the headwater streams with steep slopes during rainstorms of short duration and high intensity following dry antecedent periods as Storm 4 and Storm 5.

5.3. Hydrochemical regimes on DOC and FAM dynamics

Our results suggest that the DOC vs. FAM relationships can also be useful to understand the DOC dynamics from slopes to streams in humid and temperate mountainous headwater catchments including only the first order stream. Then, the hydrochemical regimes which were obtained in our study from the DOC vs. FAM relationships with respect to stream flow in the headwater catchments, together with slope hydrology, are diagrammed in Figure 7. The main flows contributing DOC and FAM to the streams, that is, the flow pathways along the slope, can be distinguished by examining the DOC vs. FAM relationships in Figures 4 and 6.

Hirano et al. (2009) showed that, by use of hydrograph separation method based on the change in the silicon concentration in stream flow and rainfall, subsurface flow from the deep soil and groundwater discharge were the main components of baseflow in both catchments. Thus, DOC and FAM close to the baseflow trends in both catchments (Figure 7a) were mainly contributed by groundwater discharge (GW in Figure 7). Simultaneously, the DOC vs. FAM relationships distributed above the baseflow trend lines (Figure 7a) may reflect the fact that the DOC and FAM resulted both from biomat flow which was prominent in the coniferous catchment and from near-surface flow in the deciduous catchment (n-Sur in Figure 7).

In contrast, the DOC vs. FAM relationships distributed along the soil extract trend lines (Figure 7a) strongly reflect that DOC and FAM were transported mainly by subsurface flow through soils (Sub in Figure 7), where the DOC concentration but not the F-FAM was relatively high. In Storm 2, which was the small-scale rainstorm following relatively wet antecedent periods, the DOC vs. FAM relationships shifted to the bottom of the soil extract trend lines with higher DOC concentration than that following relatively dry antecedent periods of Storm 1 (Figures 6a and 6d). This fact shows that relatively deep subsurface flow (Sub-d in Figure 7) may have mainly produced the high DOC concentration in stream flow during the small rainstorms following wet antecedent periods.

The DOC vs. FAM relationships between the trend lines of baseflow and soil extracts (Figure 7a) presumably reflect DOC and FAM transport resulted from the contribution of subsurface and groundwater flow (Sub+GW in Figure 7), and sometimes reflect the contribution of near-surface or biomat flows (n-Sur) by their shift toward the high F-FAM relevant to DOC concentration.

6. Conclusions

To understand the dynamics of DOC and FAM transport into streams in mountainous headwater catchments, we conducted hydrological observations and analyses in a coniferous and deciduous catchment. The following characteristics of DOC and FAM transport in the mountainous headwater catchments were inferred:

1) DOC and FAM transport, including in soil extracts, baseflow, and biomat flow in the mountainous headwater catchments was clearly characterized by the difference in the ratio of change in F-FAM to that in DOC concentration (F-FAM/DOC).

2) The F-FAM/DOC ratio in the soil extracts was high in the coniferous catchment (4.91), but low in the deciduous catchment (4.14). It was higher in the baseflow and biomat flow (about 6 in both catchments) than in the soil extracts.

3) High F-FAM/DOC ratios in the baseflow were inferred to originate from groundwater discharge without humic acid like materials and biomat flow during rainstorms, whereas low F-FAM/DOC ratios in stormflow were inferred to result from DOC and FAM by subsurface flow through shallow soil.

4) Shallow soil usually and strongly contributed the DOC transport into the headwater streams in both catchments during the rainstorms. However, during the rainstorms, FAM was sometimes predominantly transported by biomat flow in steep slopes. Thus, biomat flow or near-surface flow may explain the predominant FAM transport in the headwater streams, especially during high intensity rainstorms following relatively dry antecedent periods.

These findings show that the soil organic matter component depending on differing vegetation and knowledge of preferential flow paths of rapid runoff from slopes to streams (i.e., in micro-topographic unit) are essential for understanding the primary hydrochemical processes related to DOC (and also FAM) dynamics in mountainous headwater catchments with steep slopes.

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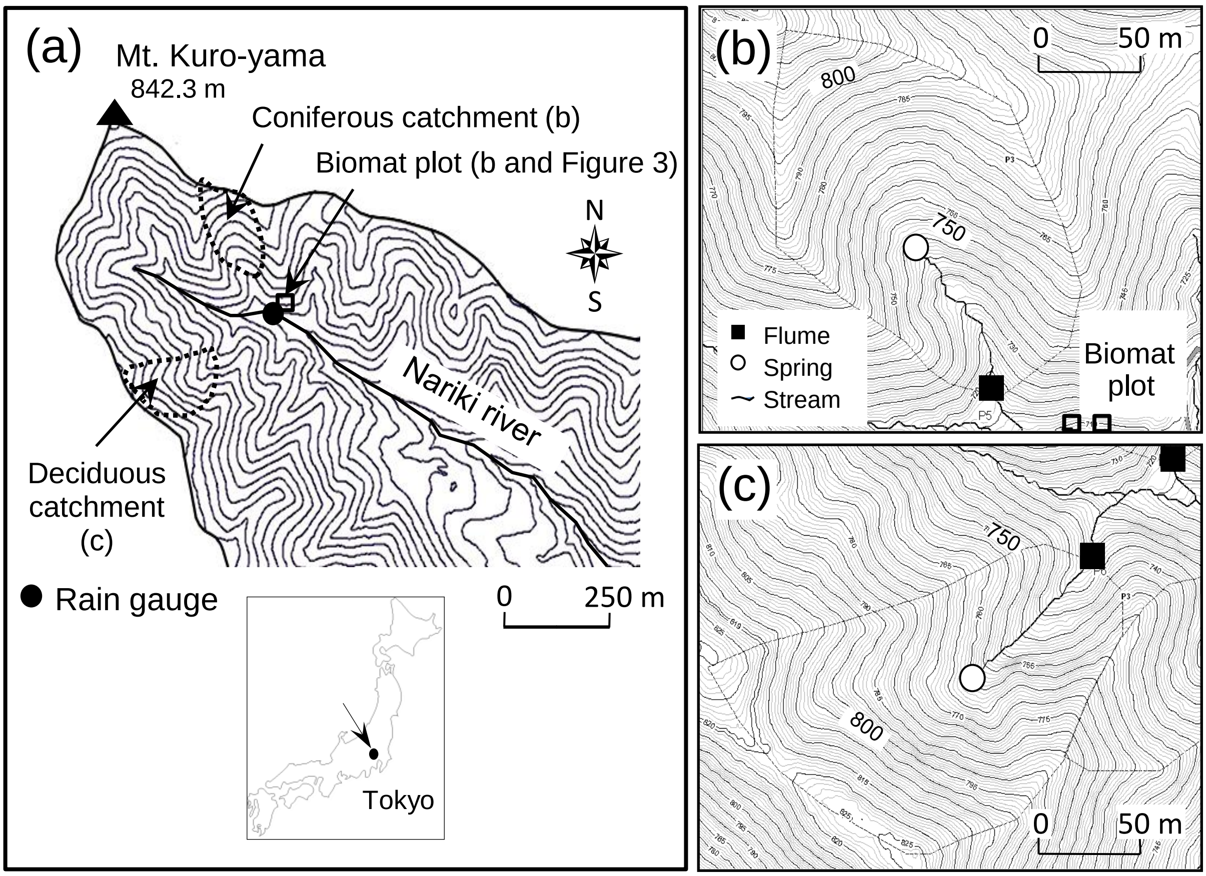

Figure 1. Location and topographic maps of the Nariki catchment and headwater catchments. (a) Nariki catchment, (b) Coniferous catchment, (c) Deciduous catchment

Contour intervals of the Nariki catchment (a) and headwater catchments (b and c) are 10 and 5 m, respectively.

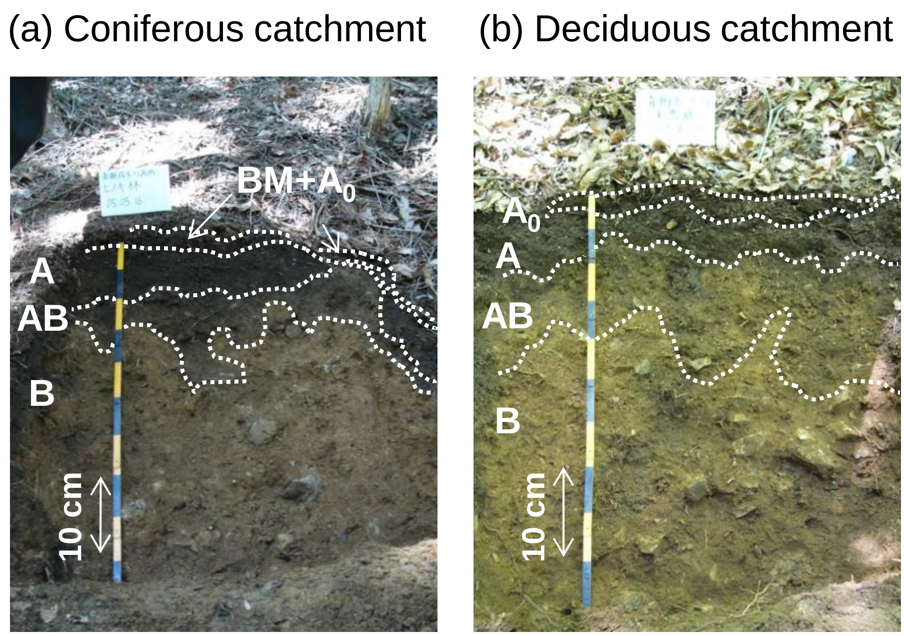

Figure 2. Shallow soil profiles at the mid-slopes of the headwater catchments (photographed by Dr. K.Tamura of Tsukuba University).

Soil horizon was classified according to the definition by the Food and Agriculture Organization of the United Nations. BM: Biomat that is permeated by the dense root networks and detritus; The maximum thickness of the biomat was about 3 cm in the coniferous catchment, whereas the biomat was indistinguishable in the deciduous catchment.

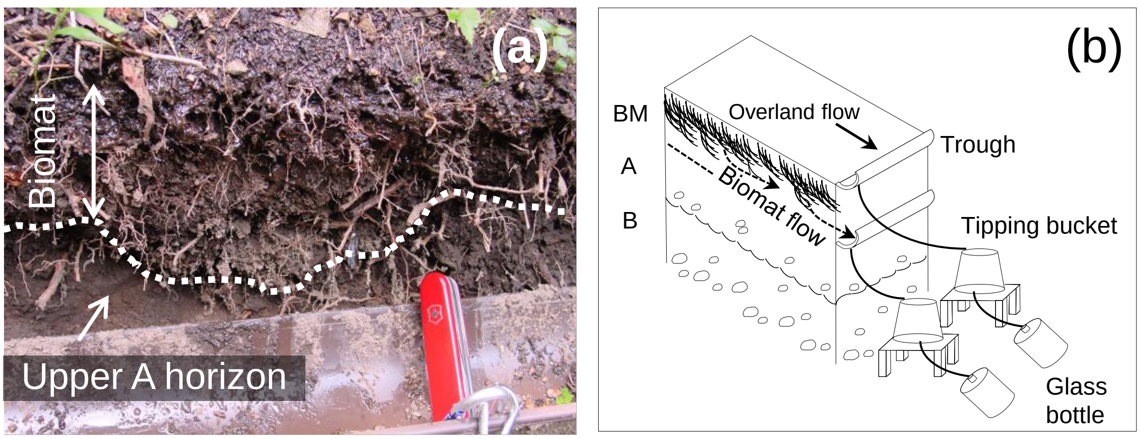

Figure 3. A photograph of the biomat developing in the coniferous forest (a) and a schematic illustration showing the observation devices for biomat flow sampling (b). The length of the knife in the photograph is about 10 cm. BM : Biomat

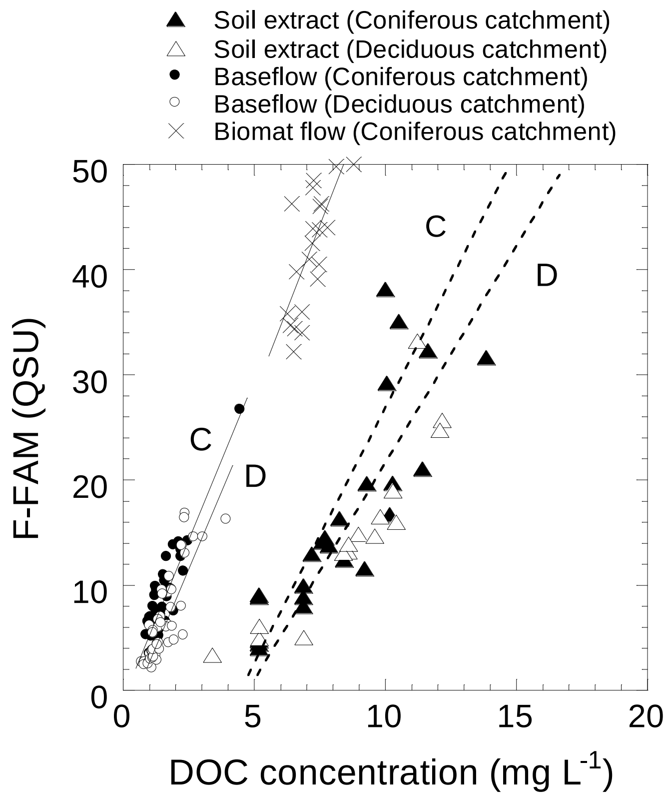

Figure 4. Relationship between the dissolved organic carbon (DOC) concentration and normalized fluorescence intensity of fulvic acid like materials (F-FAM) in baseflow (low stream flow during no rainfall), biomat flow, and soil extracts (modified after Endo et al., 2006). C: Coniferous catchment, D: Deciduous catchment

The data on soil extracts and baseflow were measured in 2005 and some supplementary data on the soil extracts were measured in 2009. The data on biomat flow were measured during summer rainstorms in 2009. The data on soil extracts and biomat flow were corrected for the inner filtering effect. Linear correlation coefficients in the coniferous and deciduous catchments are 0.84 ($p<0.0001$) and 0.89 ($p<0.0001$) in soil extracts and 0.90 ($p<0.0001$) and 0.84 ($p<0.0001$) in baseflow, respectively, and it is 0.73 ($p<0.0002$) in biomat flow. As the correlation coefficients were calculated, the data at DOC > 22 mgL^{-1} and F-FAM > 120 QSU were removed because of attenuation of the FAM spectra of the water samples due to high FAM concentration.

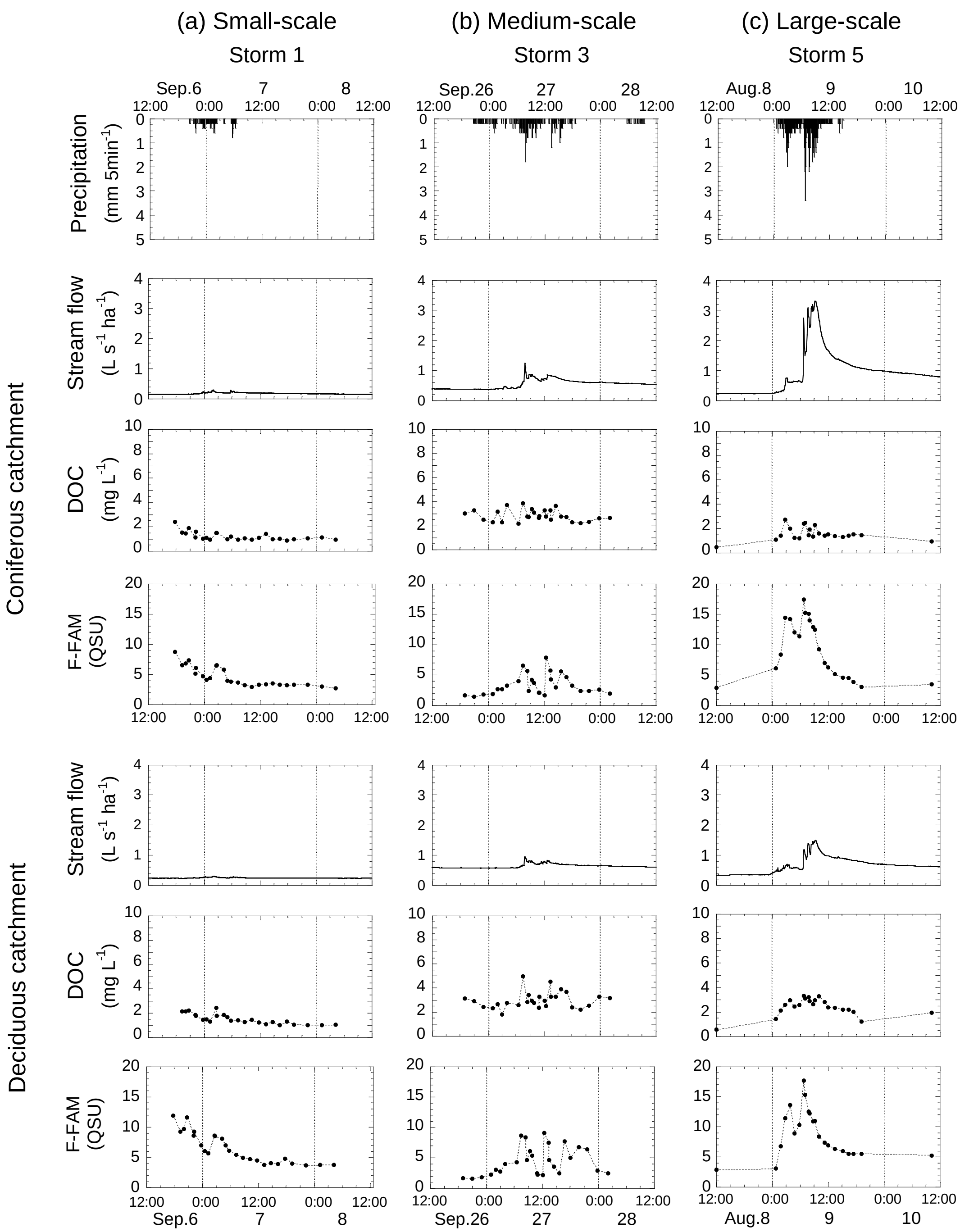

Figure 5. Temporal changes in rainstorm precipitation, specific stream flow, dissolved organic carbon (DOC) concentration, and normalized fluorescence intensity of fulvic acid like materials (F-FAM) during the representative rainstorms in 2006.

Total precipitation was 16.2, 40.4, and 77.2 and the antecedent conditions were relatively dry, wet, and dry in Storm 1, 3, and 5, respectively.

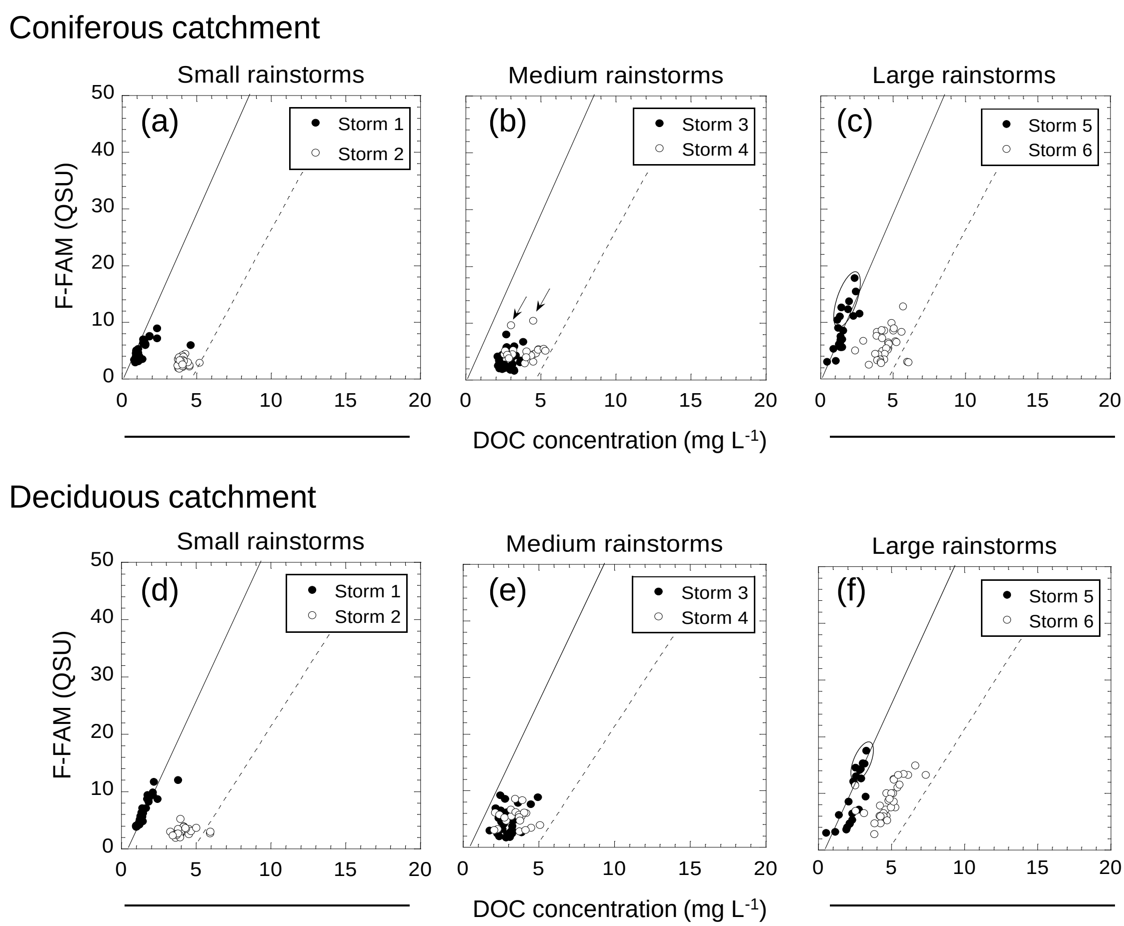

Figure 6. Relationships between the dissolved organic carbon (DOC) concentration and normalized fluorescence intensity of fulvic acid like materials (F-FAM) during the six rainstorms.

Solid and dashed lines respectively show the correlation lines of baseflow and soil extracts shown in Figure 4. The arrows and circles show the high F-FAM relative to the DOC concentration.

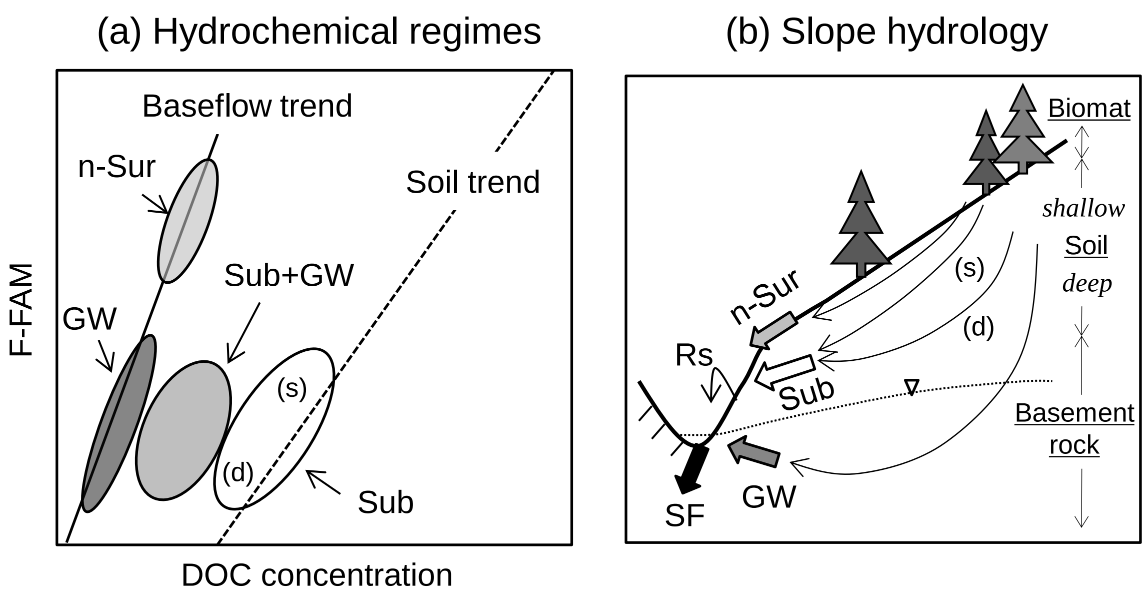

Figure 7. Schematic diagrams related to the hydrochemical regimes for the relationships between dissolved organic carbon (DOC) concentration and normalized fluorescence intensity of fulvic acid like materials (F-FAM) in headwater streams during rainstorms (a), together with slope hydrology showing the types of main flow contribution and flow path (b). SF: Stream flow, GW: Groundwater flow, Sub: Subsurface flow, (s): relatively shallow subsurface flow, (d): relatively deep subsurface flow, n-Sur: Near-surface flow including biomat flow, Rs: Rain splash.

Table 1 Hydrological conditions of the observed rainstorms.

Rainfall frequency shows the potential number of rainy days during a year relevant to the same storm magnitude in total precipitation, which were calculated from the Automated Meteorological Data Acquisition System (AMEDAS) data at Ohme City from 1976 to 2009. API-7: Antecedent precipitation index (total amount of rainfall) for past 7 days, API-14: Antecedent precipitation index for past 14 days

Storm event	Total precipitation (mm)	Rainfall duration (hour)	Rainfall frequency (days yr^{-1})	API-7 (mm)	API-14 (mm)	Baseflow prior to storms ($L\ s^{-1} ha^{-1}$)	
						Conif.	Decid.
Small-scale rainstorms							
Storm 1 (Sep.6-7, 2006)	16.2	9	28.5	0.8	27.6	0.15	0.23
Storm 2 (Sep.17-18, 2006)	22.8	12	28.5	124.0	145.0	0.96	1.42
Medium-scale rainstorms							
Storm 3 (Sep.26-28, 2006)	40.4	24	8.2	2.4	95.6	0.46	0.46
Storm 4 (Oct.23-25, 2006)	48	40	28.5	8.6	11.6	0.24	0.38
Large-scale rainstorms							
Storm 5 (Aug.8-10, 2006)	77.2	9	1.2	0	0.6	0.18	0.35
Storm 6 (Jul.14-16, 2007)	117.4	48	2.9	16.0	37.0	0.12	0.12